



Designation: B764 – 04(Reapproved 2009)

Standard Test Method for Simultaneous Thickness and Electrode Potential Determination of Individual Layers in Multilayer Nickel Deposit (STEP Test)¹

This standard is issued under the fixed designation B764; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method closely estimates the thickness of individual layers of a multilayer nickel electrodeposit and the potential differences between the individual layers while being anodically stripped at constant current density.^{2,3}

1.2 This test method does not cover deposit systems other than multilayer electroplated nickel deposits.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*⁴

B456 Specification for Electrodeposited Coatings of Copper Plus Nickel Plus Chromium and Nickel Plus Chromium

B504 Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 This procedure is a modification of the well-known coulometric method of thickness testing (Test Method **B504**). It is also known as the anodic dissolution or electrochemical stripping method.

¹ This method is under the jurisdiction of ASTM Committee B08 on Metallic and Inorganic Coatings and is the direct responsibility of Subcommittee B08.10 on Test Methods.

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² For discussion of this test, see Harbulak, E. P., "Simultaneous Thickness and Electrochemical Potential Determination of Individual Layers in Multilayer Nickel Deposits," *Plating and Surface Finishing*, Vol 67, No. 2, February 1980, pp. 49–54.

³ U.S. Patent 4,310,389. Assignee: The Chrysler Corp., Highland Park, MI 48203.

⁴ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2 Coulometric thickness testing instruments are based on the anodic dissolution (stripping) of the deposit at constant current, while the time is measured to determine thickness. As commonly practiced, the method employs a small cell that is filled with an appropriate electrolyte, and the test specimen serves as the bottom of the cell. To the bottom of the cell is attached a rubber or plastic gasket whose opening defines the measuring (stripping, anodic) area. If a metallic cell is used, the rubber gasket also electrically insulates the test specimen from the cell. With the specimen as the anode and the cell or agitator tube as the cathode, a constant direct current is passed through the cell until the nickel layer is dissolved. A sudden change in voltage between the electrodes occurs when a different metallic layer starts to dissolve.

3.3 Each different metal or species of the same metal requires a given voltage to keep the current constant while being stripped. As one nickel layer is dissolved away and the next layer becomes exposed, there will be a voltage change (assuming a constant current and difference in the electrochemical characteristics of the two nickel layers). The elapsed time at which this voltage change occurs (relative to the start of the test or previous voltage change) is a measure of the deposit thickness.

3.4 At the same time, the amplitude of the voltage change can be observed. That is, the ease (or difficulty) with which one layer can be dissolved or stripped with reference to another layer can be compared. The lower the voltage needed the more active the metal or the greater the tendency to corrode preferentially to a more noble metal adjacent to it.

3.5 Where the metallic layers are of such a similar nature that change of the stripping voltage is small, there can be problems in detecting this change if the voltage between the deplating cell (cathode) and the sample (anode) is measured. As the sample is dissolved anodically, cathodic processes are occurring on the deplating cell (cathode) surface that can also give rise to voltage changes, due to alterations of the cathode surface, thus obscuring the anode voltage change. This difficulty can be avoided by measuring the potential of the dissolving anodic sample with respect to an unpolarized third electrode (reference) placed in the cell. By recording this

potential any difference in electrochemical activity between layers is more readily detected. The equipment may be calibrated against standards with known STEP values.

3.6 The thickness of any specific nickel layer may be calculated from the quantity of electricity used (current multiplied by time), area dissolved, electrochemical equivalent of nickel, anode efficiency, and density of the nickel layer.

3.7 Commercial instruments using this principle are available. They are usually a combination coulometric and STEP instrument. Reference standards are available to calibrate the instrument. The STEP Test, as is the Coulometric Test, is rapid and destructive to the coating.

4. Significance and Use

4.1 The ability of a multilayer nickel deposit to enhance corrosion resistance is a function of the difference in the electrode potentials of the nickel layers (as measured individually at a fixed current density in a given electrolyte versus a reference electrode) and the thicknesses of the layers. The potential differences must be sufficient to cause the bright nickel or top layer to corrode preferentially and sacrificially with respect to the semi-bright nickel layer beneath it.

4.2 This test procedure allows the measurement of these potential differences directly on an electroplated part rather than on separate foil specimens in such a way that time determines the thickness of each layer, while the potential difference between nickel layers is an indication of the corrosion resistance of the total nickel deposit.

4.3 The interpretation and evaluation of the results of this test should be by agreement between the purchaser and the manufacturer.

NOTE 1—This test may be used as a quality assurance test of the multilayer nickel coatings applied in production. It should be understood that due to many factors that influence the progress of corrosion during actual use of the part, the performance of different multilayer nickel deposits in the test cannot be taken as an absolute indicator of the relative corrosion resistance of these deposits in service.

5. Apparatus

5.1 Composition of the Electrolyte⁵:

Nickel Chloride (NiCl ₂ ·6H ₂ O)	300g/L
Sodium Chloride (NaCl)	50g/L
Boric Acid (H ₃ BO ₃)	25g/L
pH	3.0 ^A

^A The pH may be adjusted with diluted hydrochloric acid or sodium hydroxide, as required, and is more critical than the composition of the electrolyte.

Prepared in Purified Water—Type IV or better as specified in Specification **D1193**.

5.2 *Constant Current Source*—This should supply a constant current that can be varied between 0 and 50 mA (typical 25 to 35 mA). A current of 30 mA corresponds to a stripping rate of 7.8 μm/min at 100 % current efficiency when used with a gasket providing 0.08 cm² stripping area. (This is achieved

⁵ Electrolyte can be obtained commercially that meets the requirements of this test.

with the solution stated in 5.1.) Most commercial coulometric thickness testers can be used as the current source.

5.3 *Electrolyte Agitation Source*—All commercial coulometric thickness testers incorporate a means to agitate the solution. It is possible to purchase these types of units separately, if so desired, to be used externally in conjunction with other power supplies.

5.4 *Recorder*—Any time-based recorder with an input impedance of at least 1.0 MΩ and capable of running at approximately 0.5 mm/s (3 cm/min) can be used.

5.5 *Deplating Cell*—The cell may be similar in construction to commercially available coulometric deplating cells. It is usually a cup-shaped cell of either 316 stainless steel, copper-nickel alloy, or plastic that engages a round rubber or plastic gasket to the work piece or sample. The opening through the cell and gasket allows contact of the electrolyte to the test specimen and defines the stripping area.

NOTE 2—A coulometric deplating cell could be constructed of plastic using a cylindrical stainless steel or copper-nickel alloy sheet cathode located in the larger upper area of the cup. The advantages of such a cell are the prevention of whisker growth and the choking off of the small bore opening, and the ease of cathode removal for cleaning or replacement.

5.6 *Reference Electrode*—Either silver or platinum wire of approximately 1.5 mm in diameter can be used. Silver is probably the better choice due to its ability to form a silver-silver chloride electrode when used in a chloride containing electrolyte. The tip of the reference electrode should extend so that the distance between the tip of the electrode and the bottom of the agitator tube is approximately 5 mm.

NOTE 3—It is necessary to condition the silver electrode before using in order to form the silver-silver chloride surface. This is easily done by anodically treating approximately a 75-mm length of wire in 1 N hydrochloric acid solution for 10 to 15 s using 35-mA anodic current. This will form a gray film on the wire, which should always be present. Once the gray film is formed, it is not necessary to repeat the conditioning treatment unless the film has been removed. It may be advisable, however, to recondition the electrode after a prolonged period of inactivity or when the electrode has been allowed to remain dry for an extended period of time. Drying off the electrode should be avoided by immersion in either the hydrochloric acid conditioning solution, the step test solution, or distilled water when not in use.

NOTE 4—A ceramic junction reference electrode that does not require conditioning is available commercially.

5.7 *Millivolt Meter (optional)*—When using a sensitive and well-calibrated recorder, a millivolt meter is not necessary. If one is desired, however, any sensitive, high-input impedance meter can be used. A standard pH meter with a millivolt setting would be satisfactory. The meter should have a range from 0 to 2000 mV. If a millivolt meter is used which has low-output impedance facilities, it can be used in parallel to drive the recorder and will serve as a buffer amplifier. Most laboratory pH meters have such output terminals.

6. Procedure

6.1 Set up equipment as recommended by the manufacturer. If necessary, turn on the recorder and the millivolt meter and allow them to warm up.

6.2 If chromium is present on the nickel surface, remove it with concentrated hydrochloric acid. Make sure the nickel surface is clean. Rinse well and dry off the surface.

NOTE 5—Chromium can be removed by using the coulometric deplating cell as is done on many commercial coulometric testers. If this is done, secure the cell and gasket to the test piece as in 6.3 and 6.4 but do not insert the electrode assembly. Fill the cell with a common test stripping solution for chromium (Test Method B504) and hook up only the cell and test piece to the power supply. Apply the current until all the chromium has been removed. A dense blanket of bubbles on the surface of the sample indicates that all the chromium is removed. Remove the stripping solution from the cell without moving or disturbing the seal of the gasket to the test surface. Wash the cell three times with purified water (Type IV or better as specified in Specification D1193) and once with the step test solution. Proceed to 6.5.

6.3 Position the test specimen in a secure horizontal position so that the chromium-stripped nickel surface is directly beneath the cell gasket.

6.4 Lower the coulometric deplating cell assembly; secure by sealing the gasket to the nickel surface. A flat test area of approximately 10 mm in diameter is desirable but not required. The criterion is that there be no leakage of the electrolyte. If leakage does occur, discontinue test and start a new one.

6.5 Fill the coulometric deplating cell to the appropriate level with the step test solution making sure that no air is trapped within the solution.

6.6 Lower the reference electrode assembly into the coulometric deplating cell, if necessary. The positioning of the reference electrode should be such that the distance from the end of the electrode to the test specimen is reproducible to within 1 mm and be held constant throughout the test.

NOTE 6—The insertion depth of the electrolyte agitation tube which includes the reference electrode is important and should always be the same. The difference of potential rather than the absolute potential is the important measurement.

6.7 Check all electrical connections. Make sure all connections are secure and that no corrosion exists at the contact points and that all contact points are secure.

6.8 Start the recorder (turn on milliamperemeter, if used). The recorder must be calibrated in order to determine the thickness of the nickel layers. This may be accomplished by using commercially available thickness standards or by applying Faraday's Law. The latter requires information about the current, corroding area, electrochemical equivalent of nickel, density of nickel, efficiency, and the time base of the recorder (see 6.11).

6.9 Turn on the constant current source and agitator, which in turn will start the deplating reaction. Continue recording until the surface underlying the nickel is reached. This end point can be recognized graphically by a sudden change in voltage. If the basis metal is zinc, iron, or steel, the voltage will decrease; if it is copper or brass, the voltage will increase.

6.10 Stop the test by turning off the agitator, constant current source, recorder, and milliamperemeter. Remove the electrode assembly, if necessary, and empty the cell of the stripping solution. Wash the cell three times with purified water (Type IV or better as specified in Specification D1193) before continuing to the next test.

6.11 This test is based on a measured current-time relationship necessary to remove a given amount of nickel from a specific area.

Example: if the constant current source produces 30 mA, the recorder time base is 30 mm/min, and the deplating area is 0.08 cm², it would take 19.2 s to deplate 2.5 μm of nickel. The chart would travel 9.6 mm. A general equation that may be used is as follows:

$$\frac{(SL)(A)(I)}{(0.303)S} = T \quad (1)$$

where:

SL = chart scan length, mm,
S = chart speed, mm/min,
I = cell current, mA,
A = deplating area, cm,
T = nickel thickness, μm, and
0.303 = constant calculated from the electrochemical equivalent and density of nickel.

NOTE 7—Commercial units are available that will modify and may simplify the above procedure.

7. Factors Affecting the Accuracy of the Method

7.1 *Excessive Metal Build-Up in Coulometric Deplating Cell*—Excessive buildup of deposited nickel or the formation of “whiskers” on the inside of the coulometric deplating cell (cathode), especially near the gasket hole, can cause erratic results and produce “noisy” curves. When buildup is observed, remove it completely according to the manufacturer's instructions or as follows:

7.1.1 If a metallic cell is used as a cathode:

7.1.1.1 Ream with a round, fine file. (A drill or reamer may be used.)

7.1.1.2 Soak for 15 to 20 s in a solution of four parts concentrated sulfuric acid and one part concentrated nitric acid. If 316 stainless steel is used for the cell, it may be soaked in concentrated nitric acid until all nickel is dissolved.

7.1.1.3 Rinse in water (Type IV or better as specified in Specification D1193) and dry.

7.1.1.4 Repeat 7.1.1.1 to 7.1.1.3 as many times as necessary to remove all metallic buildup. This cleaning process should be done after every ten tests or more frequently, if necessary.

NOTE 8—It has been found that giving the coulometric deplating cell (cathode) a nickel strike prior to using will help prevent erratic buildup or treeing around the gasket hole and cleaning will not be required as often.

7.1.2 If a metallic agitator tube is used as a cathode:

7.1.2.1 Place a stainless steel or nickel plate under the gasket, lower the cell, and rinse it with DI water.

7.1.2.2 Fill the cell with 2 to 2.5 M H₂SO₄, reverse the polarity of the current and strip the nickel from agitator tube. A cleaning current of about 55 mA for about 45 s should suffice. If the nickel is not completely removed, drain the cell, refill it with H₂SO₄, and repeat the cleaning.

7.1.2.3 Wash the cell thoroughly with water.

7.1.2.4 If the tube still looks coated, remove the coating by rubbing the agitation tube with a soft rubber eraser, followed by washing with water.

7.2 *Reference Electrode Preparation*—If the electrode has not been used for a day or has been allowed to dry for a period of time, one or two conditioning runs will have to be made prior to running a meaningful test. (See Note 2.)